EVALUATION OF A SORBENT-BASED PRECONCENTRATOR FOR ANALYSIS OF VOCS IN AIR USING GAS CHROMATOGRAPHY — ATOMIC EMISSION DETECTION

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ABSTRACT

A Hewlett-Packard 5890 gas chromatograph and 5921A atomic emission detector (AED) were used to determine volatile organic compounds (VOCs) at part-per-billion-by-volume levels in ambient air samples which were preconcentrated by using the Dynatherm ACEM 900 sorbent-based preconcentrator. Several combinations of multisorbent sampling tubes and focusing tubes were tested. Mixtures of 51 VOCs including 10 polar compounds were prepared in humidified scientific-grade air and were used to evaluate the system with regard to compound recoveries, linearity of compound concentration with varying sample volume, and the optimum volume of purge gas needed to remove water from the sorbent before thermal desorption. The automated, unattended operation of the system was also evaluated by allowing the instrument to sample indoor air at intervals of approximately 1 h over a 24-h period.

Because individual elements are detected by the AED, the hydrogen response due to water may be monitored concurrently with the response of other elements. This allowed a thorough investigation of the effect of water vapor on the carbon, chlorine, and bromine response for those compounds in the standard mixtures which coelute with water. Also, the relative amount of water vapor still present in the sample after various drying techniques were employed was easily monitored. These results and the results of the experiments mentioned above are discussed in this paper.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Currently, the U.S. Environmental Protection Agency is evaluating automated gas chromatographic systems (autoGCs) for use in network monitoring stations.[1] Desirable features of these systems include (1) the need for little or no liquid nitrogen, (2) the capability for unattended, continuous operation, (3) the capability for drying the sample stream without removing polar volatile organic compounds (VOCs) and (4) easy deployment in the field. The autoGC system being evaluated in our laboratory utilizes a Dynatherm Automated Continuous Environmental Monitor (ACEM) Model 900 sorbent-based sample preconcentrator and a Hewlett-Packard 5890 GC and 5921A Atomic Emission Detector (AED). The AED has been a useful and interesting detector for the laboratory evaluation of the system but has never been considered

suitable for field deployment because of the fragility of the GC-AED interface and support gas requirements.

EXPERIMENTAL

A Dynatherm Analytical Instruments, Inc. (Kelton, PA) ACEM 900 for sample preconcentration and thermal desorption is interfaced to a Hewlett-Packard (HP, Avondale, PA) 5890 GC which is equipped with an HP 5921A AED. The ACEM 900 is a sorbent-based system which employs two tubes; one sorbent tube collects sample and a second, narrower sorbent tube focuses the sample prior to thermal desorption onto the capillary column. A Dynatherm External Sampling Module is used to load sample onto the collection tube from a canister or to pull ambient air through the tube by using a vacuum pump. Helium may be used to purge water from the collection tube prior to desorption of the sample onto the focusing tube. The 1-m × 0.20-mm deactivated fused-silica transfer line which connects the ACEM 900 to the GC column was heated to 200 °C. A 60-m × 0.32-mm × 5-μm DB-1 capillary column (J & W Scientific, Inc., Rancho Cordova, CA) was used for the experiments discussed here, and the GC oven temperature was programmed as follows: 6 min at 30 °C, an 8 °C/min ramp to 240 °C, and a 10 min hold at 240 °C. For the analyses, the AED transfer line and cavity block were heated to 250 °C, and the AED was programmed to monitor responses of emission lines of carbon at 496 nm, hydrogen at 486 nm, chlorine at 479 nm, and bromine at 478 nm.

Challenge gas mixtures for the experiments included 6-L canister samples of a mixture of 10 ppbv of the 41 VOCs on the EPA Compendium Method TO-14 target list[2] in humidified air at ~50% RH. The canisters were prepared[3] from a cylinder containing 1–2 ppm of each compound in nitrogen (Alphagaz, Walnut Creek, CA). Also used were canister samples of a mixture of 10–20 ppbv of 10 polar compounds (methanol, ethanol, isopropanol, butanol, acetone, methyl ethyl ketone, acetonitrile, acrylonitrile, methyl methacrylate, and ethyl acrylate in humidified air at ~50% RH) which were prepared from cylinders containing 10 ppm of the compounds in nitrogen (Scott Specialty Gases, Plumsteadville, PA). Mixtures of C_2–C_6 compounds at concentrations of 15–100 ppm in nitrogen (Scott Specialty Gases) were also used to spike the tubes. This was accomplished by moving the collection tube from the ACEM 900 to a Dynatherm Model 10 tube conditioner and injecting the sample from a gastight syringe into a stream of nitrogen flowing at 50 cm^3/min through the tube. The collection and focusing tube combinations (Dynatherm Analytical Instruments, Inc.) tested are presented in Table I.

Initially, the effect of different helium purge volumes (used to remove water from the collection tube) on the response of VOCs was investigated. In these experiments, a 480-cm^3 sample of the 41-compound mixture was collected on the sorbent tube from a 6-L canister by using a 0–500-sccm mass flow controller (MFC, Tylan General, Torrance, CA) set at 80 cm^3/min. The tube was then purged with 26 cm^3/min of helium; the helium purge volumes used were 0, 50, 100, 250, 500, and 1000 cm^3. The collection tube was normally held at 40 °C for these experiments, although some experiments were repeated with the tube at 55 and 65 °C. Sample was desorbed from the collection tube onto the focusing tube for 3 min at 200 or 300 °C, followed by 2 min in cool mode (in which helium continues to flow through the tube in the desorb position while the tube is cools down from the desorb temperature). Then, the focusing tube was heated to 350 °C, as indicated by a thermocouple located outside the tube, for 3 min to desorb sample onto the GC column.

The linearity of response of the 41 VOCs and the polar compound mixture was investigated by collecting sample volumes of 250, 500, 1000, and 2000 cm^3. Again, an MFC set at 80 cm^3/min was used to load the samples from 6-L canisters onto the collection tube, and the tube was purged with 500 cm^3 of helium to remove residual water. Tube heating and cooling parameters were the same as those listed above.

Table I. Tube combinations

Tubes (Sorbent* and Focusing)	Experiments			
	Vary He Purge Volume	Linearity	Retention of C_2 Compounds	24-h Monitoring
Tenax-TA/Ambersorb XE-340/Charcoal + Tenax-TA/Silica gel/Ambersorb XE-340/ Charcoal	X	X	X	X
Carbotrap C/Carbotrap B/Carboxen 1000 + Tenax-TA/Silica gel/Ambersorb XE-340/ Charcoal	X	X	X	X
Tenax-TA/Carboxen 1000 + Carbotrap B/Carboxen 1000	X		X	
Tenax-TA/Ambersorb XE-340/Charcoal + Carbotrap B/Carboxen 1000	X		X	

*6-mm-o.d. sorbent tubes.

The retention of ethane, ethylene, and acetylene on different collection and focusing tube combinations was investigated by spiking 6-mm-o.d. and 10-mm-o.d. tubes with 1–10 cm^3 of the C_2–C_6 gas mixtures as discussed above. In addition to the tube combinations in Table I, nine tube combinations were evaluated by using one of each of the following 10-mm-o.d. collection tubes: Tenax-GR/Carboxen 1000, Tenax-GR/Carboxen 1000/Spherocarb, or Tenax-GR/Carboxen 1000/Carbosieve SIII; the collection tube was used with one of each of the following focusing tubes: Carbotrap B/Carboxen 1000, Tenax-GR/Spherocarb, or Tenax-GR/Carbosieve SIII. In these experiments, the collection tube was held at 40 °C and desorbed at 300, 325, or 350 °C. The heat and cool mode times were varied from 1 to 3 min and 0 to 2 min, respectively, to determine the optimum operating conditions for retention of C_2 compounds. The focusing tube was then desorbed for 3 min at 300 or 350 °C.

To test the unattended, repetitive operation of the ACEM 900, the unit was set to collect ~20 samples of ambient indoor air during a 24-h period. A sampling pump was used to pull sample across the sorbent tube by using the external sampling module. Sample volumes of 250 cm^3 of air were collected, and the tube was flushed with 500 cm^3 of helium. The collection tube was heated to 200 or 300 °C for 3 min and then cooled for 2 min prior to desorbing the focusing tube for 3 min at 350 °C.

RESULTS AND DISCUSSION

Because the GC-AED is capable of monitoring the responses of individual elements, the effect of water vapor on the responses of Cl, Br, and C for the 41 VOCs could be easily investigated. Of the four tube combinations evaluated for recovery of the 41 VOCs as a function of varying the helium purge volume, two combinations worked satisfactorily. When the Tenax/silica gel/Ambersorb/charcoal focusing tube was used in combination with either the Tenax/Ambersorb/charcoal or the Carbotrap C/Carbotrap B/Carboxen 1000 sorbent tubes, the large amount of water left on the sorbent tube at low-helium purge volumes resulted in decreased responses for lighter compounds eluting simultaneously with the broad water peak. The responses of compounds which eluted after the water had eluted were not affected. Examples of this are presented in Figures 1a and 1b. When the Carbotrap B/Carboxen 1000 focusing tube was used in combination with either the Tenax/Carboxen 1000 or Tenax/Ambersorb/charcoal sorbent tube,

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substantially less water was retained, and the response of the lighter compounds was not suppressed at lower helium purge volumes. This is illustrated in Figure 1c.

The results of the linearity tests for both the 41-compound mixture and the polar mixture showed good linearity for most compounds for up to 1 L of sample collected. Some compounds, such as benzyl chloride, *m*-, *p*-, and *o*-dichlorobenzene, chlorobenzene, and 1,1,2,2-tetrachloroethane collected on the Tenax/Ambersorb/charcoal tube and the polar compounds collected on the Carbotrap C/Carbotrap B/Carboxen 1000 tube, were observed to be linear for up to 2 L of sample collected. Bromomethane became nonlinear when more than 500 cm^3 of sample was collected on the Tenax/Ambersorb/charcoal tube, possibly because at higher sample volumes the bromomethane travels into a sorbent layer from which it is not easily desorbed. The linearity results for two representative compounds are presented in Figure 2.

For retaining the C_2 compounds, the optimum operating parameters were determined to be heating the collection tube 2 min and cooling 0 min. When the tube was heated and cooled for 3 min and 2 min, respectively, as for the 41-compound mixture, the ethene and acetylene were not retained. To obtain better separation of the light compounds for the determination of recoveries, the GC oven was programmed as follows: -50 °C for 2 min, 8 °C/min to 150 °C, 150 °C for 3 min. The best tube combinations for recovering the C_2 compounds were Tenax-GR/Carboxen 1000/Carbosieve S-III or Tenax-GR/Carboxen 1000/Spherocarb sorbent tubes coupled with a Tenax-GR/Carbosieve S-III focusing tube. With these tube combinations, recoveries were estimated to be ~100% for ethane, ~70% for ethene, and ~30% for acetylene when a 500-cm^3 helium purge volume was used. Other tube combinations tested retained less, if any, of the ethylene and acetylene when purged with 500 cm^3 of helium. A sorbent tube combination that will retain 100% of acetylene and ethene has not yet been identified.

The ACEM 900 was easily programmed for unattended, continuous operation, and the system ran without fail for the two 24-h experiments. Figure 3 is a plot of the concentration of dichloromethane observed in the laboratory air vs. time of day for the experiment using the Tenax/Ambersorb/charcoal sorbent tube and the Tenax/silica gel/Ambersorb/charcoal focusing tube combination.

CONCLUSIONS

The Dynatherm ACEM 900 preconcentrator offers several attractive features. It is reliable and easy to operate. The instrument requires no cryogenic liquids and may be operated unattended, and the helium purge option allows water to be removed from the sample without removing polar VOCs. These features contribute to the ACEM 900's promise as a preconcentrator for use in an autoGC network for monitoring polar and nonpolar VOCs. However, the instrument must be further evaluated to compare the results of these experiments with those of a cryogenic preconcentrator and to challenge the system with the very low (low-part-per-billion-by-volume) levels of VOCs found in ambient air.

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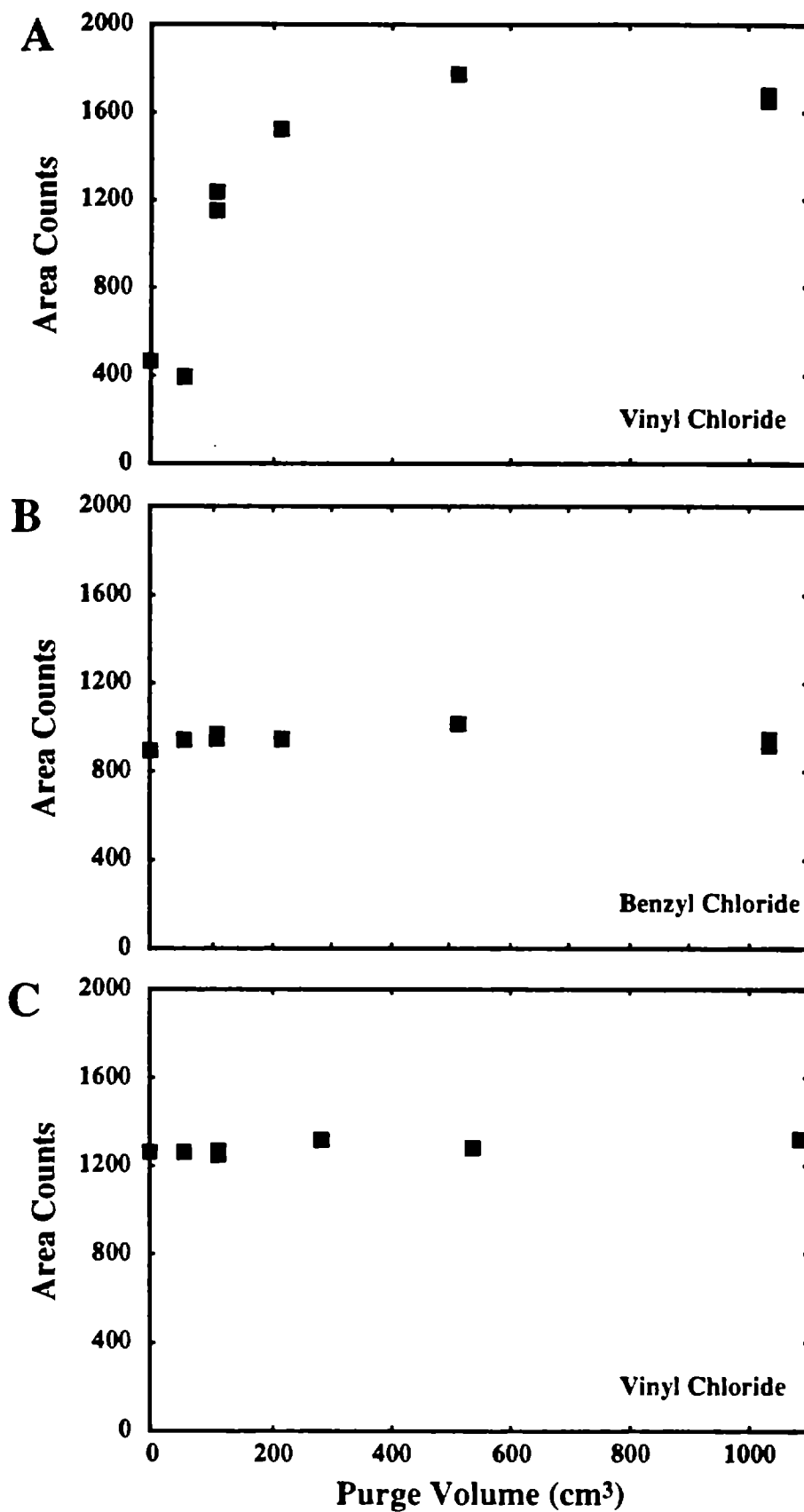
Figure 1. Effect of purge volume on Cl response with different sorbent tube — focusing tube combinations: Tenax/Ambersorb/charcoal — Tenax/silica gel/Ambersorb/charcoal (A) and (B), and Tenax/Carboxen 1000 — Carbotrap B/Carboxen 1000 (C).
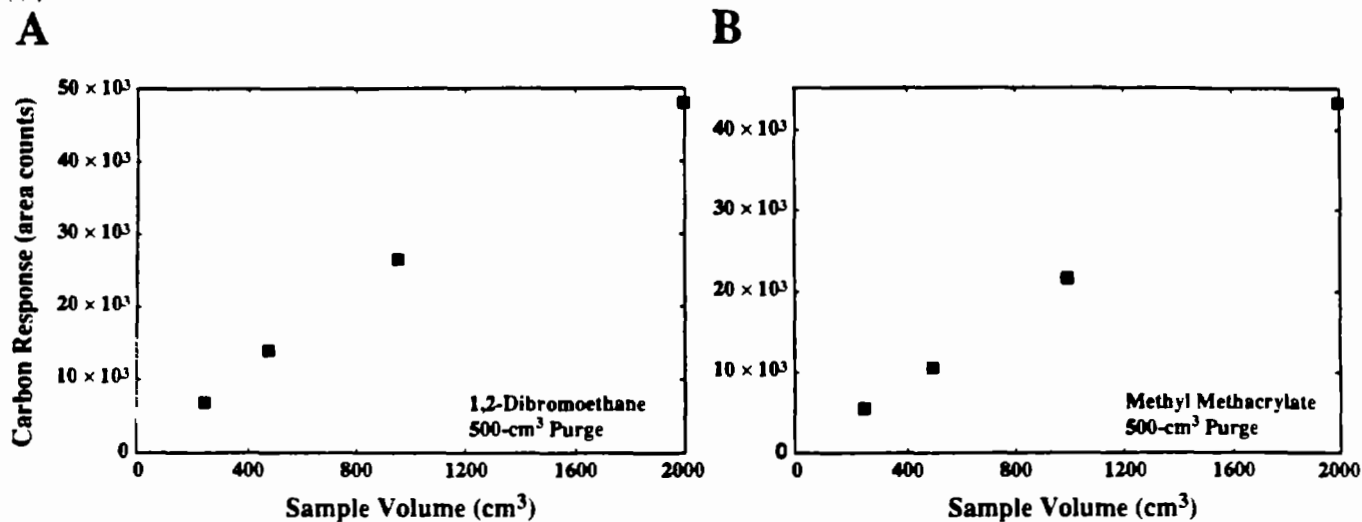
Figure 2. Linearity test with (A) Tenax/Ambersorb/charcoal – Tenax/silica gel/Ambersorb/charcoal tubes and (B) Carbotrap C/Carbotrap B/Carboxen 1000 – Tenax/silica gel/Ambersorb/charcoal tubes.
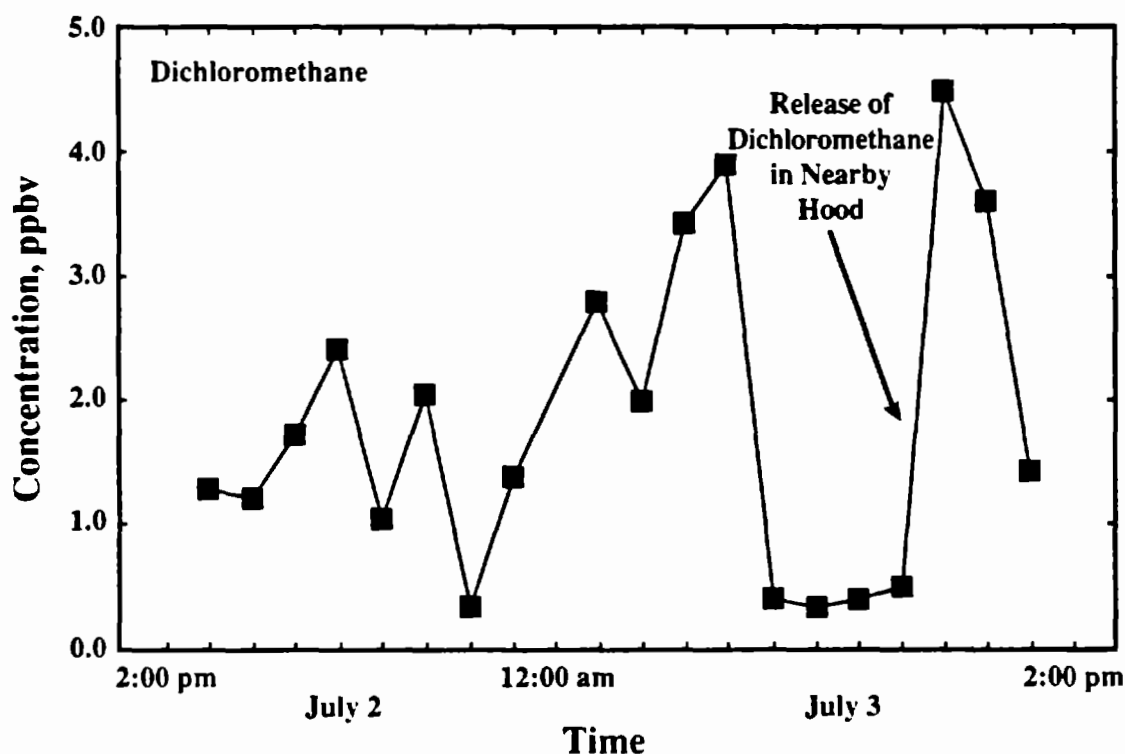

Figure 3. Diurnal variation in concentration with the ACEM 900 and the Tenax/Ambersorb/charcoal sorbent tube – Tenax/silica gel/Ambersorb/charcoal focusing tube combination.

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/A-92/251	2.	3. PB93-121077		
4. TITLE AND SUBTITLE Evaluation of a Sorbent-Based Preconcentrated for Analysis of VOCs in Air Using Gas Chromatography-Atomic Emission Detection		**5.REPORT DATE** April 15, 1992		
		6.PERFORMING ORGANIZATION CODE		
7. AUTHOR(S) K. D. Oliver, E. H. Daughtrey, Jr. and W. A. McClenny		**8.PERFORMING ORGANIZATION REPORT NO.**		
9 PERFORMING ORGANIZATION NAME AND ADDRESS ManTech Environmental Services Research Triangle Park, NC 27711		**10.PROGRAM ELEMENT NO.** A101C-C18-01		
		11. CONTRACT/GRANT NO. 68-DO-0106		
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research and Exposure Assessment Lab - RTP Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		**13.TYPE OF REPORT AND PERIOD COVERED** Proceedings - 4/91 - 4/92		
		14. SPONSORING AGENCY CODE EPA/600/09		

15. SUPPLEMENTARY NOTES

This work establishes design parameters for the use of carbon-based multisorbent tubes used as preconcentrators of volatile organic compounds when sampling ambient air. The multisorbents were tested in a two stage configuration with a primary tube for collection and a secondary tube for focusing of the VOCs collected in the primary tube. A system consisting of a Dynatherm ACEM 900 preconcentrator, Hewlett-Packard 5890 gas chromatograph and 5921A atomic emission detector was used to establish VOC trapping and release efficiency and the optimum purge gas volume to remove water from the primary tube. Results will be used to design an automated gas chromatograph to meet the VOC monitoring requirements of Title I and Title III of the CAAA of 1990.

16. ABSTRACT

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		**b.IDENTIFIERS/ OPEN ENDED TERMS**	**c.COSATI**
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC		**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21.NO. OF PAGES** 7
		20. SECURITY CLASS *(This Page)* UNCLASSIFIED	**22. PRICE**